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MINERAL FILLED POLYMERS

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1. Abstract

The use of mineral fillers increases continuously. The incorporation of the filler into the polymer results in new materials. The properties of these composites are determined by the characteristics of the components, composition, interfacial interactions and structure. Both aggregation and orientation of anisotropic filler particles affect strongly composite properties. Mineral filled polymers are used in a wide range of applications, mostly in fields in which increased stiffness and heat resistance are required. Although CaCO_3 , talc and glass fibers are used in the largest quantities, new fillers (natural fibers) and novel composites (nanocomposites) also gain increasing importance in this field.

2. Keywords: particulate fillers, short fibers, nanofillers, layered silicates, carbon nanotubes, graphene, wood flour, natural fibers, interfacial interactions, aggregation, orientation, application, automotive

3. Introduction

Particulate filled polymers are widely used in many fields of application. With the exception of PVC, mostly technical and technological reasons justify the introduction of fillers, since a separate compounding step increases the price of the composite considerably. The combination of a filler with a polymer results in a new material with changed properties. Some of these changes are advantageous [improved stiffness, higher heat deflection temperature (HDT), better heat conductivity], while others are less favorable (decreased deformability and impact, wear

of the processing equipment). As a consequence, an optimum of various properties must be found during the development of a new material and the selection of the type and grade of the filler is always an important part of the process. In this communication a brief account is given about the most important fillers used in plastics, the method of incorporation, the factors influencing the properties of the composites, and finally some areas are mentioned in which mineral filled polymers are used in considerable quantities.

4. Fillers

Some information about the most important particulate fillers are listed in the following paragraphs, for more detailed information refer to handbooks (Katz and Milewski 1978, Wypych 1999) and monographs (Rothon 2003).

4.1. CaCO_3

The application of CaCO_3 exceeds the use of any other filler by one order of magnitude in polymers. This mineral exists in three crystalline modifications (calcite, aragonite, vaterite), but only calcite has practical importance. It can be found in large quantities all over the world, but minerals mined at different locations differ considerably in purity, size of the crystals and origin, which all influence their use as fillers. In nature it can be found in three different forms: as limestone, chalk and marble. Limestone is a consolidated sedimentary rock formed by the deposition of shells and skeletons of marine organisms, chalk is soft-textured limestone laid down in the cretaceous period and consists of nanofossils, while marble is metamorphic limestone

formed under high pressure and temperature. CaCO_3 is prepared also via synthetic routes, however, the price of precipitated CaCO_3 is considerably higher than that of the ground mineral, thus it can be used only in specific applications.

4.2. Talc

The chemical composition of pure talc is $\text{Mg}_3(\text{Si}_4\text{O}_{10})(\text{OH})_2$; it is a secondary metamorphic mineral. The filler consists of platelets. The layers of the particles are bonded only by secondary, van der Waals forces, cleavage occurs very easily also under the conditions of usual thermoplastic processing technologies. Talc is the softest mineral, its Mohs hardness is 1. Its surface is rather hydrophobic, active hydroxyl groups can be found only at broken edges and surfaces, thus the surface modification of the filler is difficult. It reinforces polymers due to its platelet like geometry and has a strong nucleation effect in some crystalline polymers, especially in polypropylene (PP), further increasing its stiffening effect.

4.3. Short Fibers

Short glass fibers represent a transition between anisotropic mineral fillers and long fiber reinforcements. They are introduced mostly into engineering thermoplastics, but considerable quantities are used also in PP and in sheet molding compounds (SMC). Lately short carbon fiber reinforced composites also appeared on the market. The proper surface modification of the fiber is crucial in all fiber reinforced composites.

4.4. Other Fillers

Kaolin is used in various forms in polymers (china clay, calcined clay). The anisotropic particle geometry of wollastonite and mica reinforces the polymer. The latter is applied more extensively in the USA and Canada due to the closer location of mining facilities. Barite filled polymers, mostly PP, have excellent vibration damping properties due to the high density of this filler. Wood flour and natural fibers (flax, hemp, jute, sisal, etc.) are applied in increasing quantities mostly in composites for the building and the automotive industry. The water absorption of these fillers creates problems in processing and application. Lately, increasing interest is shown in layered silicates, mostly in montmorillonite. The nanocomposites prepared from these minerals are claimed to possess unique properties at reduced filler content. since expectations have not been fulfilled and only a few practical applications were found for composites prepared with layered silicates, recently the focus of attention has moved from them first to carbon nanotubes and then to graphene (Mittal 2015, Spitalsky 2010, Hu 2014). Some characteristics of a few mineral fillers are collected in Table 1.

5. Compounding

The polymer and the filler must be homogenized prior to the manufacture of a product. The thorough homogenization of the components is the minimum condition of easy processing and application. Insufficient homogenization leads to aggregation. Aggregates cause surface blemish and deteriorate all properties especially impact strength, because they initiate cracks under external loading.

Compounding is mostly done in twin screw extruders. The major advantages of this equipment are continuous operation, high productivity and flexibility. Machine configuration and processing conditions can be adjusted according to the properties of the processed material. Both the screw and the barrel of these machines are constructed from segments and can be assembled to produce the necessary conditions for efficient mixing. High shear must be used for the homogenization of particulate filled polymers to avoid aggregation, but low shear and intensive mixing is preferred in the case of shear sensitive polymers (PVC) and fillers (starch), as well as glass (GF) and carbon (CF) fibers. The attrition of fibers leads to the loss of their reinforcing effect and generally to the deterioration of composite properties.

6. Factors Influencing the Properties of Filled Polymers

The properties of mineral filled polymers are determined by the characteristics of the components, composition, interaction and structure. All four factors can vary in a wide range thus allowing the preparation of tailor made composites.

6.1. Component Properties

Important properties of the matrix polymer are its chemical composition and melt viscosity. The first determines the strength of interaction with an uncoated filler, while the second influences the shear stresses developing during homogenization. The extent of aggregation, as well as the smallest particle size, which can be used in a polymer, are determined by the relative magnitude of adhesion and shear forces acting in the melt during homogenization (Pukánszky and

Fekete 1999, Móczó and Pukánszky 2008). The mechanical properties of the matrix polymer strongly influence the micromechanical deformation processes taking place under the effect of external load. Large stresses develop in a stiff matrix, the dominating deformation mechanism is usually debonding. In such cases yield stress and strength decrease with increasing filler content (Fig. 1). In a softer polymer (LDPE) the introduction of the same filler results in true reinforcement, yield stress and strength increase with increasing amount of filler.

Numerous filler characteristics influence the properties of the composites. Chemical composition (purity) affects color and stability. However, mechanical properties and performance are determined mainly by particle size, particle size distribution, specific surface area and shape. An optimum particle size exists for each polymer and processing technique. Large particles debond easily from the matrix under loading, while small particles tend to aggregate; both processes deteriorate composite properties significantly. Specific surface area determines the contact surface between the filler and the polymer thus the amount of interphase formed. Surface free energy (surface tension), hardness and thermal properties are other filler characteristics which influence the production or application of mineral filled polymer composite parts.

6.2. Composition

The stiffness of the composite increases, while its price often decreases with increasing filler content, thus significant effort is concentrated on the introduction of the largest possible filler loadings into the polymer. Since other properties deteriorate at the same time, composition must be optimized for the combination of all, or at least the most important properties.

Although occasionally a linear correlation is claimed between stiffness and filler content, theory predicts non-linear relationship (Nielsen 1978). The overall belief is that tensile yield stress and tensile strength decrease with increasing filler content, when fillers with nearly spherical shape are used. The composition dependence of these properties are strongly influenced also by particle characteristics. As Fig. 1 shows true reinforcement can be achieved with fillers in a soft polymer, and if particle size is sufficiently small the same effect is observed in PP (see Fig. 2) or PVC as well (Pukánszky 1995, Móczó and Pukánszky 2008). The effect of anisotropic fillers depends on the orientation of the particles. Deformability, yield strain and elongation-at-break always decrease with increasing filler content. Impact resistance often exhibits a maximum at a certain filler content, which depends on the characteristics of the filler, but also on interfacial interactions (Pukánszky and Maurer 1995). The maximum is a consequence of several competitive effects, the debonding of the filler during deformation leads to energy consumption, while increasing filler loadings result in increased stiffness and decreased impact resistance. Most other properties (heat conductivity, HDT, hardness) are more or less proportional to the filler content of the composite.

6.3. Interfacial Interaction

This factor strongly influences the properties of polymer composites. Mostly weak van der Waals forces act between the polymer and the filler in thermoplastics, but they are sufficiently strong to bond the two components. The adsorption of the polymer on the filler surface leads to the formation of an interphase in which molecules have decreased mobility. The existence of the interphase is proved by the increase of composite viscosity, yield stress and strength with

increasing specific surface area of the filler. The effect of interactions depend on the size of the contact surfaces (specific surface area of the filler) and the strength of the interaction. Smaller particles have larger surface area leading to increased yield stress (Fig. 2).

Interfacial interactions are often modified, the most frequently used methods can be classified into four categories. **Non-reactive coating** (surfactants) leads to the decrease of particle/particle and matrix filler interaction. The latter results in decreased strength and increased deformability, occasionally to increased impact resistance, while the former to improved processability, homogeneity and appearance. **Reactive treatment** (coupling), which assumes the formation of covalent bonds with both components, is difficult in most thermoplastics due to the lack of reactive groups on the polymer. Reactive coupling is easier in thermoset matrices, frequently a considerable amount of filler or reinforcement is added to them. A good example is the SMC containing short glass fibers and a large amount of CaCO_3 . The introduction of **functionalized polymers** into the composite was shown to improve adhesion and increase yield stress as well as tensile strength in the case of various fillers, from CaCO_3 , through wood flour and magnesium hydroxide to glass fibers (Fig. 3). The technology is used mostly in polyolefins, and especially in PP, but occasionally also in other polymers. In multicomponent polymer systems containing a filler and two polymers, a special morphology may form in which one of the polymer components **encapsulates the filler**. Naturally such a structure is accompanied by significantly modified interaction and properties (Móczó and Pukánszky 2008, Pukánszky 1995).

6.4. Structure

Particulate filled polymers are believed to have a simple structure consisting of uniformly dispersed particles in a homogeneous matrix. However, structure related phenomena are at least as important in composites as in polymer blends. Two important structural phenomena must be always kept in mind when filled polymers are prepared and applied. Small particles tend to form aggregates, which deteriorate properties. Above a certain specific surface area the aggregation tendency of spherical, uncoated fillers becomes significant. This critical surface area depends on several factors including the viscosity of the polymer, filler characteristics, processing technology, etc. The orientation of anisotropic particles determines their reinforcing effect. Anisotropy (aspect ratio) alone is not sufficient to achieve reinforcement, the proper orientation of the particles is necessary to increase stiffness and strength.

7. Application

Large amounts of CaCO_3 is used in PVC, both in plasticized (cable, flooring) and rigid (pipes, fittings, profiles) products. Although at a much lower level, CaCO_3 , but also talc, is often introduced into PP as well. Such composites are used in the automotive industry as bumpers, air-filter covers or heater boxes, as household articles like garden furniture, washing machine soap dispensers, etc. Artificial paper and breathable films are prepared from HDPE containing considerable amounts of CaCO_3 . Sheet and bulk molding compounds (SMC, BMC) represent the most important application in thermosets, products prepared from them are used in construction, in the automotive industry, etc. The intended use of the new class of mineral filled polymers,

nanocomposites, was mostly in structural applications. These composites was claimed to possess improved mechanical properties, decreased gas permeation and flame retardancy and enhanced properties were expected to be accompanied by considerable weight savings. As it turned out most of the expectations have not been fulfilled and these materials are used mainly in niche applications in small quantities. Polymers reinforced with carbon nanotubes and graphene are relatively new, they might find application in special areas like additional reinforcement to long fiber reinforced composites, modification of matrix properties, antistatic and electrically conducting polymers, etc.

8. Summary

The use of mineral fillers increases continuously. The incorporation of the filler into the polymer results in new materials. The properties of these composites are determined by the characteristics of the components, composition, interfacial interactions and structure. The latter factor is often neglected during the development of mineral filled polymers, although both aggregation and orientation of anisotropic filler particles affect strongly composite properties. Mineral filled polymers are used in a wide range of applications, mostly in fields in which increased stiffness and heat resistance are required. Although CaCO_3 , talc and glass fibers are used in the largest quantities, new fillers (natural fibers) and novel composites (nanocomposites) also gain increasing importance in this field.

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12. References

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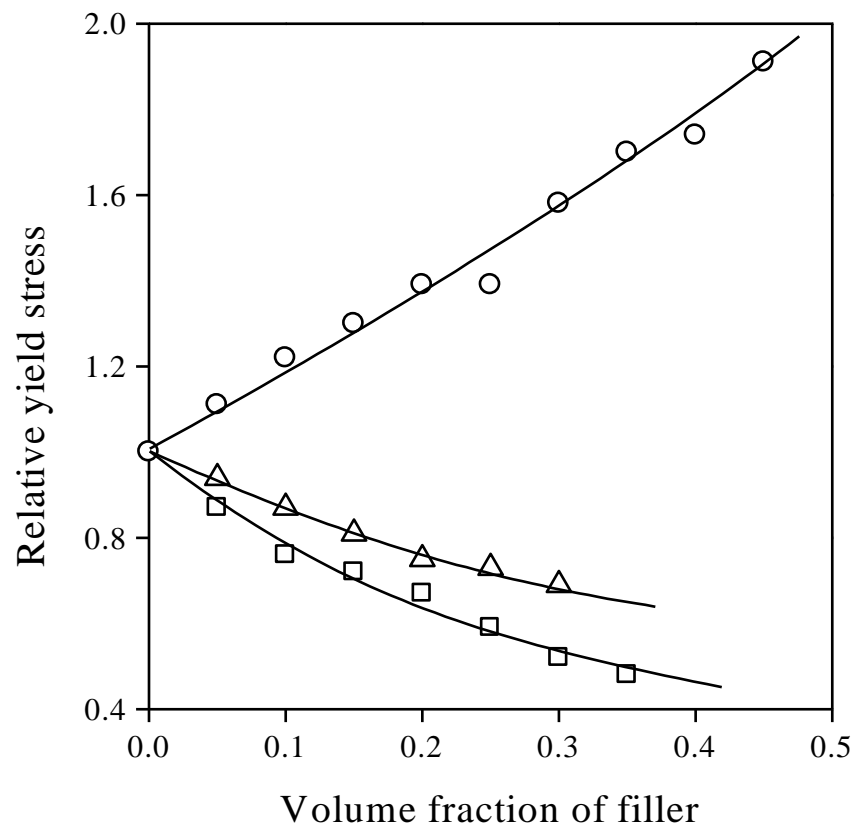
Table 1 Composition and properties of particulate fillers

Filler	Composition	Density (g/cm ³)	Mohs hardness	Shape
Calcium carbonate	CaCO ₃	2.7	3	sphere
Talc	Mg ₃ (Si ₄ O ₁₀)(OH) ₂	2.8	1	plate
Kaolin	Al ₂ O ₃ ·2SiO ₂ ·2H ₂ O	2.6	2.5-3.0	plate
Wollastonite	CaSiO ₃	2.9	4.5	needle
Mica	KM(AlSi ₃ O ₁₀)(OH) ₂	2.8	2.0-2.5	plate
Barite	BaSO ₄	4.5	3.5	plate

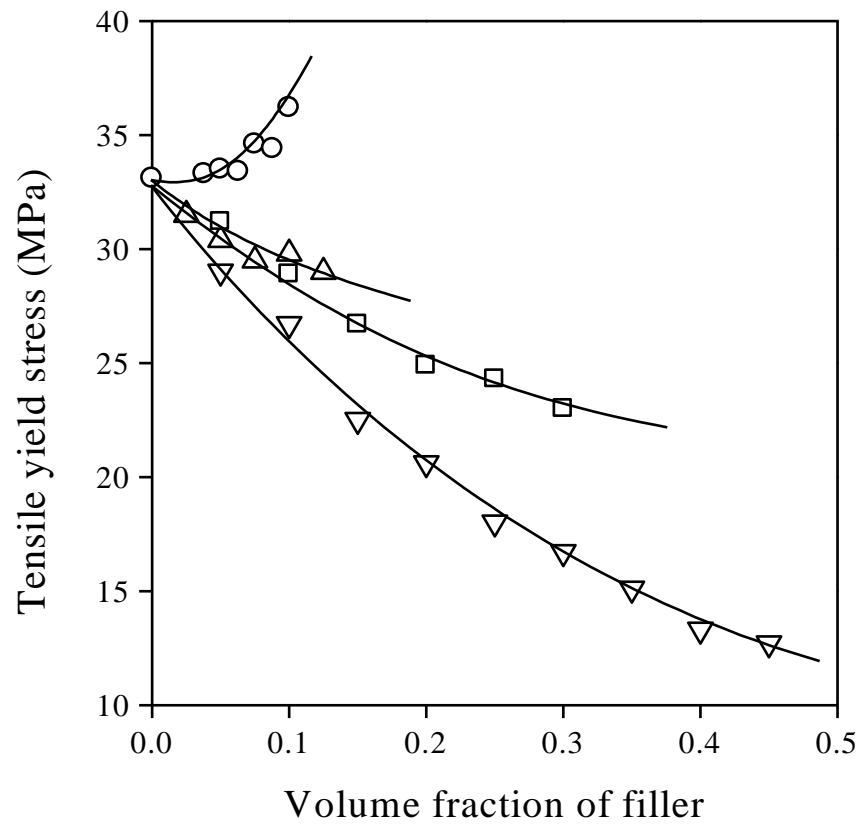
Captions

- Fig. 1 Effect of matrix properties on the reinforcing effect of a particulate filler (CaCO_3 , $3.6\text{ }\mu\text{m}$). (\circ) LDPE, (\triangle) PP, (\square) PVC
- Fig. 2 Effect of particle size on the tensile yield stress of PP composites. Particle diameter: (\circ) $0.01\text{ }\mu\text{m}$, (\triangle) $0.08\text{ }\mu\text{m}$, (\square) $3.3\text{ }\mu\text{m}$, (∇) $58\text{ }\mu\text{m}$
- Fig. 3 Modification of interfacial interaction in mineral filled composites; effect on the tensile yield stress of PP/ CaCO_3 ($3.6\text{ }\mu\text{m}$) composites. (\circ) uncoated, (\triangle) increased interaction (MAPP), (\square) decreased interaction (stearic acid)

Pukánszky, Fig. 1



Pukánszky, Fig. 2



Pukánszky, Fig. 3

